

Anelastic relaxation process of polaronic origin in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$: interaction between the charge stripes and pinning centers.

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The evolution of an anelastic relaxation process occurring around 80 K in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at a measuring frequency of ~ 1 kHz has been followed from $x = 0.0075$ to the overdoped region, $x = 0.2$, where it disappears. The dependence of the peak intensity on doping is consistent with a polaronic mechanism, identified with the disordered charge stripes overcoming pinning centers. A marked decrease of the peak amplitude and of the effective energy barrier for relaxation occurs at $x > 0.045$, the same doping range where a change of the stripe order from parallel to diagonal with respect to the Cu-O bonds has been observed by neutron diffraction. Both the energy barrier and peak amplitude also exhibit a rise near $x = 1/8$.

I. INTRODUCTION

Much evidence has been accumulated of the segregation of the charge carriers into fluctuating stripes in the cuprate superconductors.^{1,2,3,4,5} In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ codoped with Nd the stripes are seen by neutron diffraction as a static lattice modulation coherent with the low-temperature tetragonal (LTT) modulation;^{1,2} in the absence of a stable LTT phase, dynamic charge and magnetic correlations are observed with a spacing incommensurate with the lattice parameter, and with the direction of the modulation which changes from diagonal to parallel with respect to the Cu-O bonds when increasing doping above 6%.⁴ In addition, there are several other experimental indications that, although not providing a spatial characterization as the diffraction methods do, still are consistent with the segregation of the charge carriers into stripes.^{5,6,7,8} In particular, the anelastic spectroscopy has recently put in evidence a rise of the elastic energy loss in concomitance with the freezing of the Cu^{2+} spins into the cluster spin glass phase, which has been interpreted as the motion of the stripes between the pinning points constituted by the Sr dopants.^{9,10} It has also been shown that the dynamics of such stripes is frozen by the LTT modulation in LBCO also far from the condition $x = 1/8$ for the commensuration between lattice and stripe spacing.¹⁰ Recently, the issue has been addressed whether it is possible to observe at higher temperature the process of depinning of the stripes from the impurities.¹¹ In fact, among some anelastic relaxation processes which are observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ between 50 K and 100 K, there is one at 80 K (measured at 1 kHz) that seemed to also have the ^{139}La nuclear quadrupolar relaxation counterpart at 150 K (20 MHz).¹¹ The latter relaxation process was identified as magnetic, thereby providing evidence of simultaneous lattice and magnetic relaxation, unless due to the nearby Néel transition. Further measurements have confirmed the second alternative,¹² but this does not exclude the assignment of the anelastic relaxation to the stripe depinning. The reason why such a process, together with others, would be seen by anelastic but not by NQR relaxation is that the latter is dominated by the relaxation from the Cu spin fluctuations, while the anelastic spectroscopy is only indirectly sensitive to the spin fluctuations in case of magnetoelastic coupling.

In what follows a study is presented of the anelastic relaxation process around 80 K in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ over a wide doping range. It is shown that the process disappears in the overdoped state, as expected from a polaron-like phenomenon, and its dependence on doping is inconsistent with explanations in terms of unwanted impurities or off-stoichiometry defects; it is then discussed in terms of interaction between charge stripes and pinning centers.

II. EXPERIMENTAL

A series of ceramic samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x \leq 0.20$ was prepared by conventional solid state reaction as described in Ref. 13. After sintering, the samples were cut in bars approximately $40 \times 4 \times 0.6 \text{ mm}^3$. Interstitial O is always present in the as-prepared state of samples with low doping ($x < 0.045$), as evidenced by the anelastic spectra;^{9,14} in these cases the excess O was outgassed by heating in vacuum up to 830 K.

The complex Young's modulus $E(\omega) = E' + iE''$, was measured as a function of temperature by suspending the bars on thin thermocouple wires and electrostatically exciting their flexural modes. The frequencies $\omega_i/2\pi$ of the first three odd flexural modes are in the ratios 1 : 5.4 : 13.3 with $\omega_1/2\pi \sim 1 \text{ kHz}$ for the present samples. The elastic energy loss coefficient is commonly indicated as the reciprocal of the mechanical quality factor:¹⁵ $Q^{-1}(\omega, T) = E''/E'$, and was measured from the decay of the free oscillations or from the width of the resonance peak. The $Q^{-1}(\omega, T)$ function is related to the imaginary part of the dynamic elastic susceptibility (compliance) and therefore contains contributions from any process coupled to the measured strain ε and having spectral weight at ω . At such low frequencies only relaxation or diffusion processes are relevant; an elementary relaxation process consisting of jumps or transitions with rate τ^{-1} between states which differ in anelastic strain by $\Delta\varepsilon^{\text{an}}$ contributes with

$$Q^{-1}(\omega, T) = \Delta \frac{\omega\tau}{1 + (\omega\tau)^2}, \quad (1)$$

where the relaxation strength is $\Delta \propto (\Delta\varepsilon^{\text{an}})^2/T$. The above expression is peaked at $\omega\tau = 1$, and since the measurements are made at the resonance frequencies ω_i as a function of temperature, one finds peaks at the temperatures T_i such that $\omega_i\tau(T_i) = 1$. Therefore, measurements at different frequencies provide the temperature dependence of the rate $\tau^{-1}(T)$, which generally follows the Arrhenius law

$$\tau^{-1}(T) = \tau_0^{-1} \exp(-E/k_B T). \quad (2)$$

A process characterized by a spectrum of relaxation times may be described by the phenomenological expression

$$Q^{-1}(\omega, T) = \Delta \frac{1}{(\omega\tau)^\alpha + (\omega\tau)^{-\beta}}, \quad (3)$$

which is the Fuoss-Kirkwood expression for $\beta = \alpha < 1$,¹⁵ and reduces to the Debye formula, Eq. (1), for $\alpha = \beta = 1$. The parameter α controls the peak broadening in the low temperature region, where $\omega\tau < 1$, and β in the high temperature region.

III. RESULTS

Figure 1 presents the anelastic spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at various dopings,

measured exciting the first flexural modes at ~ 1 kHz. The peak around 150 K becomes much more intense in La_2CuO_4 free of interstitial O,¹⁴ where it can also be observed as a maximum in the ^{139}La nuclear quadrupolar relaxation rate.¹⁶ It has been associated with the collective tilting dynamics of the O octahedra in local multiwell potentials, describable as soliton-like tilt waves.¹⁶ The depression of the peak intensity and perhaps also the shift to higher temperature with increasing doping are connected with the lattice disorder introduced by Sr, which hinders the collective tilt modes; this process will not be considered further here. Another minor peak may appear near 50 K, whose behavior as a function of Sr and O doping is less regular than that of the other two processes, and this peak also will not be considered further. The interest will be focused on the peak near 80 K, indicated with an arrow; its intensity becomes rather small for $x \geq 0.08$ and completely disappears in the overdoped state $x = 0.20$. The spectra at optimal and higher doping are shown separately in Fig. 2; the step above 220, 170 and 50 K in the $Q^{-1}(T)$ curves at $x = 12.5, 15$ and 0.20 is due to the tetragonal/orthorhombic (HTT/LTO) structural transformation,¹⁴ which shifts to lower temperature with increasing doping. The curve for $x = 0.045$ has also been included, in order to render the peak near 80 K more recognizable (indicated by an arrow). The dependence of the intensity of the 80 K maximum on doping, $Q_M^{-1}(x)$, is shown in Fig. 3 in logarithmic scale, together with other concentrations not reported in Figs. 1 and 2.

Figure 4 shows a fit of the spectra of the $x = 0.015$ sample measured at three frequencies. All the peaks are fitted with the expressions (3) and (2); for the 50 K and 150 K peaks, an additional temperature dependence of the relaxation strength had to be introduced. The analysis of the 80 K peak, like in Fig. 4, can be properly carried out up to $x = 0.045$, while at higher doping the peak becomes rather small and masked by the HTT/LTO structural transition and the other peak near 50 K, so that only its height can be extracted without an appreciable error. The peak is rather broad, with a width parameter of the Fuoss-Kirkwood distribution $\alpha = \beta = 0.6 - 0.7$. The upper panel of Fig. 3 shows the dependence of the activation energy E_p on doping; the most reliable data, based on analyses like that in Fig. 4, show a decrease from $E_p/k_B = 1700$ K to 1100 K when x passes from 0.015 to 0.08, while the preexponential factor τ_0 passes from 1.4×10^{-13} s to 10^{-10} s, so that the temperature of the peak measured around 1 kHz does not change much; for this reason we will refer to the "80 K peak", but it is understood that the peak temperature is different at different frequencies. The data at $x = 0.0075$ and $x > 0.08$ have larger error bars, but sufficient to reveal a remarkable resemblance of the $E_p(x)$ curve with $\log[Q_M^{-1}(x)]$ in the lower panel,¹⁷ including a peak around $x = 1/8$.

IV. DISCUSSION

Before discussing the 80 K relaxation process in terms of stripes, the possibility should be considered that it is due to some impurities or off stoichiometry defects. The explanation in terms of foreign impurities is very unlikely in view of the dependence of the peak intensity $Q_M^{-1}(x)$ on doping (see Fig. 3). If the cause were an impurity in the starting CuO powder, like Fe, the effect should be independent of doping, or possibly depend in a monotonous way on x ; neither can a correlation be found between the $Q_M^{-1}(x)$ and x or $1 - x$, which might justify an impurity in the starting La or Sr oxides. The O off-stoichiometry has also to be considered, since it is certainly present. Interstitial O cannot be the cause of the 80 K peak, which is even suppressed at high enough O content (oxygenated or as-prepared state at low x , not shown here). Regarding the O vacancies in the CuO_2 planes, they may certainly be present in some of the outgassed samples¹⁸ with $x \leq 0.045$, but the other samples have not been outgassed because no traces of interstitial O were found in the as-prepared state. Therefore we conclude that no impurity or defect connected with off-stoichiometry can account for the $Q_M^{-1}(x)$ dependence in Fig. 3.

Instead, the dependence of the intensity of the 80 K peak on doping is fully consistent with a polaronic origin. In fact, the process should be absent in the undoped state, and indeed a steep decrease of the intensity occurs below 1.8% doping. It should also disappear in the overdoped state, where the charge carriers are in a uniform metallic state, and in fact the peak is undetectable at $x = 0.20$, after passing through a maximum around $x \sim 0.02$ and a secondary maximum near $x = 1/8$. A truly undoped state is difficult to obtain, due to the presence of both interstitial O and O vacancies. The first is readily detected by the intense $Q^{-1}(T)$ peaks due to its hopping;^{14,19} The typical content of interstitial O at $x = 0$ after sintering is¹⁸ $\lesssim 0.005$ and causes a doping of $\lesssim 0.01$; as mentioned above, the samples with $x \leq 0.045$ were subjected to an outgassing treatment, but at $x = 0$ it is difficult to completely eliminate interstitial O without also creating O vacancies in the CuO_2 planes.¹⁸ To our knowledge, the effect of these vacancies on the electric and magnetic properties has not been studied, but the anelastic spectra depend critically on the presence of such O defects in the 50 – 250 K range. For this reason, we could not obtain a sample with $x = 0$ which is at the same time completely undoped and without a peak around 80 K.

Regarding the nature of the process, if the peak were only observed at very low doping, it might be associated with a localized defect, like a small polaron hopping around a particular type of impurity, but the persistence of the peak at doping levels as high as 0.15 excludes this possibility. At high doping the only reasonable possibility of a polaronic relaxation is connected with the charge

stripes, and, since thermal activation over a barrier of $E_p \geq 0.1$ eV is required, the process must be connected to the presence of pinning centers. In fact, although the dynamics of the stripes has never been measured precisely, their motion far from pinning centers must be much faster than the average τ^{-1} of the 80 K relaxation process: the anelastic spectra at liquid He temperatures^{9,10} indicate that the mean fluctuation frequency passes through the kHz range close to the $T_g(x) \simeq 0.2$ K/ x temperature for the freezing into the cluster spin glass state. Probes with higher characteristic frequencies, like NQR and μ SR detect onset temperatures for the stripe ordering with progressively higher temperatures, up to ~ 20 K for the neutron scattering experiments,³ and the effective energy barriers for such fluctuations are in the range $E = 20 - 60$ K, as discussed in Ref. 20.

Therefore, the proposed picture is that the charge stripes may fluctuate very fast far from the pinning centers, as it appears from most experiments,^{3,5,9,10,20} but the process of depinning or overcoming the pinning centers requires the energy $E_p \geq 0.1$ eV deduced from the 80 K peak. The regularly spaced arrays of stripes are observed by diffraction well below 80 K,^{1,2,3,4} but around this temperature the stripes would already exist in a disordered state, which can be identified with the nematic stripe phase devised by Kivelson *et al.*²¹.

The task of discussing the doping dependence of the relaxation strength of this depinning process in terms of some existing model, like those of a moving dislocation or domain wall, is not obvious. In fact, such models are appropriate when interpreting the anelastic relaxation at liquid He temperatures in the cluster spin glass phase,^{9,10} where the stripes act as walls between domains with AF correlations, and the stripe motion is associated with a variation in the sizes of the adjacent domains. If an anisotropic strain is associated with the staggered magnetization within each domain, then the change of the sizes of domains with different orientations causes a change of the anelastic strain ϵ^{an} . Similarly, the movement of a dislocation is associated with the shift of a part of the crystal, and again is a source of anelastic strain. Instead, a charge stripe at 80 K does not separate domains with different anelastic strains, since at these temperatures the Cu spins are fluctuating much faster than the sample vibration frequency;⁵ therefore, it is no more appropriate to associate an anelastic strain proportional to the area swept by the stripe, as in the above models. In the present case, ϵ^{an} should be associated with the different configuration of the stripe in the pinned or unpinned state, or on either side of the pinning center. It is likely that ϵ^{an} , like the distortion coupled to the presence of holes,⁸ is mainly connected with the in-plane shear also associated with the tilts of the octahedra. Then, it is reasonable to assume that ϵ^{an} is an increasing function of the local degree of tilting of the octahedra. This would partly explain the general reduction of the relaxation strength with increasing doping, because both the in-plane shear strain and tilt angles Φ of the octahe-

dra are decreasing functions of doping.²² Note, however, that also other ingredients must determine the relaxation strength, since the marked decrease of $Q_M^{-1}(x)$ between $x = 0.05$ and 0.08 , would not be justified by the smooth $\Phi(x)$ function.²² Interestingly, the jump of $Q_M^{-1}(x)$ occurs in the doping region of the crossover from parallel to diagonal stripes,⁴ providing an additional indication that the 80 K peak is indeed associated with the stripes.

Regarding the relaxation rates $\tau^{-1}(T)$ deduced from fits like that in Fig. 4, the values of the preexponential factors, $\tau_0^{-1} = 10^{10} - 10^{13}$ s⁻¹, may seem too small for a polaronic relaxation, but are reasonable for an extended entity like the charge stripe. The most striking observation is the close similarity between the $E_p(x)$ and the $\log[Q_M^{-1}(x)]$ curves, with a sharp peak centred at $x = 0.13$, near $x = 1/8$, out of a general decrease with increasing doping. The activation energy E_p can be identified with the barrier for depinning or overcoming the pinning center and must therefore depend on the nature of this defect. Two possibilities are the Sr dopants or the twin boundaries between the two variants of the LTO domains; the latter are immobile at 80 K, since the motions of the twin walls and of the tilt waves are observed in the anelastic spectra just below the HTT/LTO transition and at 150 K respectively.¹⁴

The hypothesis that pinning is due to irregularities in the energy landscape resulting from the octahedral tilts, e.g. the twin walls and/or the substitutional disorder in the La/Sr sublattice, provides an explanation for $E_p(x)$ being a generally decreasing function of x . In fact, the decrease of the tilt angles $\Phi(x)$ implies closer minima in the multiwell potential for the octahedral tilts, smaller barriers and therefore a smoother overall potential. The rather broad distribution of relaxation rates ($\alpha = 0.6 - 0.7$ instead of 1 in Eq. 3) is also understandable in this picture, since the pinning energy would depend on the particular geometry of the local tilts. The close relationship between the $E_p(x)$ and the $\log[Q_M^{-1}(x)]$ curves can also be understood in this framework, since stripes that are more defined and associated with larger atomic displacements must result both in larger relaxation strength and larger pinning energy; in particular, the rise of both near $x = 1/8$ is consistent with the tendency of the lattice to develop an LTT modulation commensurate with the stripes,^{1,2} which makes them more well defined but also tends to pin them.

V. CONCLUSION

The anelastic relaxation process occurring in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ around 80 K for $\omega/2\pi \sim 1$ kHz has been studied over a wide doping range. All the features of this relaxation process, and notably the dependence of its intensity and activation energy on doping, confirm the earlier proposal that it is associated with disordered charge stripes interact-

ing with pinning centers. Within this interpretation, the activation energy measured from the dependence of the anelastic spectra on frequency, $E_p \sim 0.1 - 0.18$ eV, represents the energy necessary for the stripes to overcome the pinning centers, and is enhanced in correspondence with the doping $x \sim 1/8$, at which the stripe and lattice modulations become commensurate. The pinning potential can be associated with irregularities in the ordered pattern of the octahedral tilts due to the Sr dopants and/or other defects that are frozen below 100 K, like the twin walls.

ACKNOWLEDGMENTS

The authors thank Prof. A. Rigamonti for useful discussions.

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FIG. 1. Elastic energy loss coefficient versus temperature of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.015$ (1.3 kHz), $x = 0.018$ (1.0 kHz), $x = 0.045$ (0.85 kHz), $x = 0.08$ (1.0 kHz) and $x = 0.20$ (2.7 kHz). The peak attributed to the interaction between stripes and pinning centers is indicated with an arrow.

FIG. 2. Elastic energy loss coefficient versus temperature of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.045$ (0.85 kHz), $x = 0.125$ (1.5 kHz), $x = 0.15$ (1.7 kHz) and $x = 0.20$ (2.7 kHz). The peak attributed to the interaction between stripes and pinning centers is indicated with an arrow.

FIG. 3. Lower panel: intensity of the elastic energy loss peak at ~ 80 K as a function of Sr doping. Upper panel: apparent activation energy of the peak. The continuous lines are guides for the eye.

FIG. 4. Anelastic spectrum of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.015$ measured on the 1st, 2nd and 3rd flexural modes at the frequencies indicated in the figure. The continuous lines are fits as described in the text. The peak attributed to the interaction between stripes and pinning centers is indicated with an arrow.

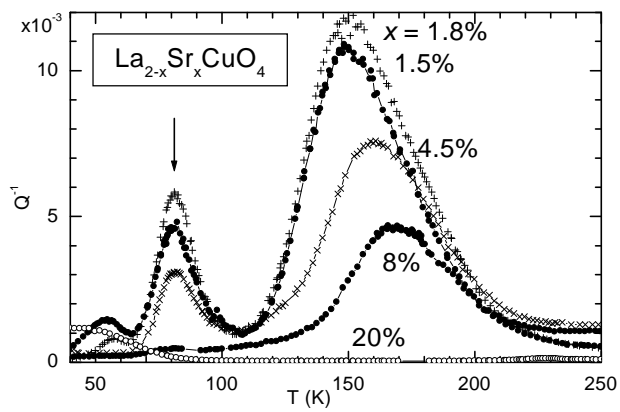


Fig. 1

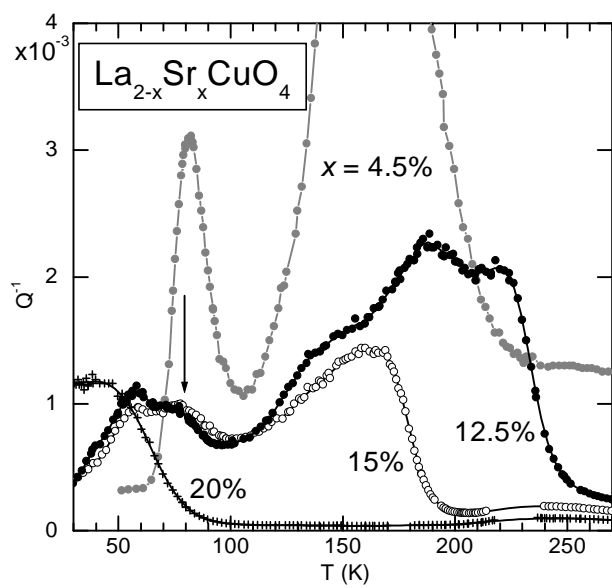


Fig. 2

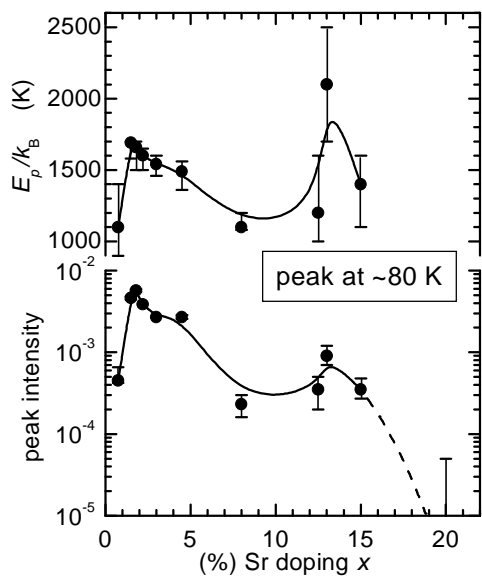


Fig. 3

Fig. 4

